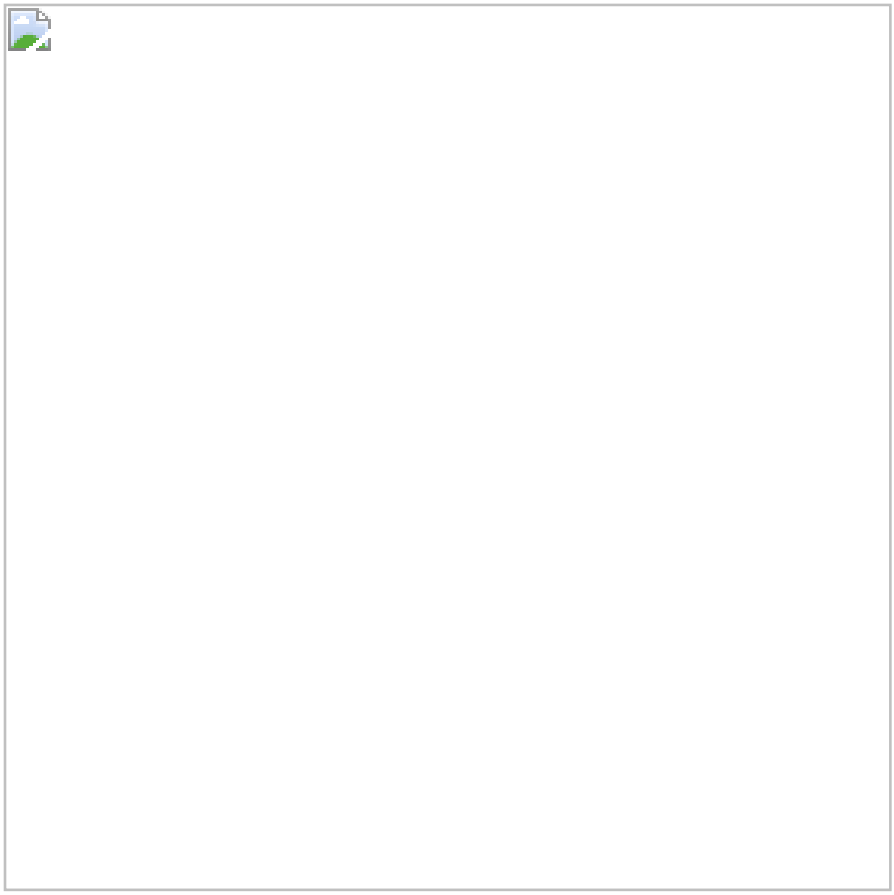

Spatial Distributions and Seasonal Variations of Dissolved Black Carbon in the Bohai Sea, China

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Spatial Distributions and Seasonal Variations of Dissolved Black Carbon in the Bohai Sea, China

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ABSTRACT

Huang, G. P.; Chen, Y. J.; Tian, C. G.; Tang, J. H.; Zhang, H.; Luo, Y. M.; Li, J., and Zhang, G., 2016. Spatial distributions and seasonal variations of dissolved black carbon in the Bohai Sea, China. *In*: Harff, J. and Zhang, H. (eds.), *Environmental Processes and the Natural and Anthropogenic Forcing in the Bohai Sea, Eastern Asia. Journal of Coastal Research*, Special Issue, No. 74, pp. 214–227. Coconut Creek (Florida), ISSN 0749-0208.

To investigate the temporal and spatial variations of dissolved black carbon (DBC) concentrations in the Bohai Sea, China, 495 seawater samples on 141 sites were collected in different water depths and seasons in six cruises from 2010 to 2014 for DBC quantification by the molecular marker method-benzene polycarboxylic acid method. The average concentration of DBC was 96.6 ± 32.9μg L^{-1} (n = 495) in the entire Bohai Sea, while it was 136.2 ± 33.7 μg L^{-1} (n = 28) in the Laizhou Bay, 131.2 ± 30.3 μg L^{-1} (n = 44) in the Bohai Bay, 86.3± 16.1μg L^{-1} (n = 66) in the Liaodong Bay, 89.6±19.8μg L^{-1} (n = 277) in the Central Bohai Basin and 57.8 ± 8.6 μg L^{-1} (n = 80) in the Bohai Strait respectively. DBC concentrations showed a distinct decreasing trend from coastal area to offshore area and from the internal Bohai Sea to the Bohai Strait in horizontal distribution although no significant differences ($p > 0.1$) was observed in the vertical water column. The average DBC concentrations of the Central Bohai Basin and the Bohai Strait in spring, summer, autumn and winter were comparable. However the DBC concentration patterns in different seasons varied significantly, such as the DBC concentrations were lower in the southern than northern of the Bohai Strait in spring, but it was inversed in autumn and winter. The seasonal variations of DBC concentration patterns followed the seasonal variations of ocean currents, suggesting that DBC would serve as a potential marker for the hydro-dynamics study.

ADDITIONAL INDEX WORDS: *Benzene polycarboxylic acid (BPCA) method, Hydro-dynamics.*

INTRODUCTION

Dissolved black carbon (DBC) is a term to describe a series of condensed aromatic compounds whose molecular structures contain four to seven aromatic rings as a core and peripheral substituted function groups, including carboxylic, hydroxyl and alkanes (Dittmar and Koch, 2006; Kim *et al.*, 2004). The aromatic core is generally believed to be formed from organic compounds during the heat-process reaction, mostly combustion (Dittmar, 2008; Dittmar and Paeng, 2009). The hydrophilic functional groups, carboxylic and hydroxyl make DBC mobile in water so that DBC is much easier to transport than BC in soil (Jaffé *et al.*, 2013; Mitra *et al.*, 2014). DBC is ubiquitous in all aquatic environments, which has been investigated in glacier melted water, river water, lake water, brackish water, sea and ocean water (Bisiaux *et al.*, 2011; Ding *et al.*, 2014; Ding *et al.*, 2015; Dittmar and Koch, 2006; Jaffé *et al.*, 2013; Kim *et al.*, 2004; Mannino and Harvey, 2004; Mitra *et al.*, 2014; Stubbins *et al.*, 2012a).

In recent decade, DBC has attracted an increasing attention due to its potential role in various environmental processes like the global carbon cycle and climatic change since its molecular structures have been confirmed by Kim *et al.* (2004). DBC is the in-

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termediate products from BC degradation, thus it reflects the reaction path for BC degradation mechanism (Hockaday *et al.*, 2006; Hockaday *et al.*, 2007). DBC is an important part of dissolved organic carbon (DOC). Estimations have shown that at least 2% of DOC in the ocean is DBC (Masiello, 1998; Dittmar and Paeng, 2009; Ziolkowski, 2010). As is known that the DOC carbon pool in the ocean is comparable to CO_2 carbon pool in the atmosphere, and DOC is deemed to be one of CO_2 sinks, so even little change of DOC carbon pool may affect the global warming (Hedges, 2002). What's more, unlike the active components of DOC, DBC is relatively inert and can stay for thousands of years in the ocean (Ziolkowski and Druffel, 2010). Long life time of DBC indicates that it plays an important role in the slow carbon cycle.

DBC is an important component of chromophoric dissolved organic matter (CDOM) which can absorb solar radiation, alter the optical environment of aquatic system and then affect the primary productivity and the structure of micro-ecosystem (Andrew *et al.*, 2013; Stubbins *et al.*, 2010; Stubbins *et al.*, 2012b). In addition, DBC is adsorbent and the chelate center, which can collect organic contaminants and heavy metal ions and then affects their transportation and bio-toxicity (Dougherty, 1996). There was evidence proofed that the main source of DBC was the BC degradation intermediate products in the terrestrial soil which mobilized into water and then migrated with water masses from surface leaching runoff to rivers and over the estuaries to the ocean (Guggenberger *et al.*, 2008; Hockaday *et al.*, 2006; Hockaday *et al.*, 2007; Masiello and Louchouarn, 2013; Ward *et al.*, 2014). Previous studies showed that the concentrations of DBC in different water bodies varied largely (Bisiaux *et al.*, 2011; Ding *et al.*, 2014; Ding *et al.*, 2013; Ding *et al.*, 2015; Dittmar and Paeng, 2009; Dittmar *et al.*, 2012b; Jaffé *et al.*, 2013; Mannino and Harvey, 2004). Although increasing investigations have been conducted on the DBC, the available data is still too sparse to well understand the biogeochemistry processes of DBC. The investigation of the potential role of DBC in the environment is only on the beginning stage, so more investigations are urgently needed.

The Bohai Sea is a semi-enclosed sea surrounded by the mainland and the Liaodong Peninsula, connecting to the North Yellow Sea through the narrow Bohai Strait (BHS) (Figure 1). It is a shallow epicontinental sea with mean water depth of 18 m, area of *ca* 7.7 × 10^4 km^2, where the deepest part (*ca* 70 m) is located in the northern Bohai Strait. The Bohai Sea is geographically composed of the Central Bohai Basin (CBHB) where the maximum water depth is approximately 30 m, and three shallow bays, the Laizhou Bay (LZB) in the south, the Bohai Bay (BHB) in the west and the Liaodong bay (LDB) in the north (Qiao, 2012; Wang *et al.*, 2014). Because of the semi-closed characteristic and owning only one water exchange path (the Bohai Strait), the water exchange ability of the Bohai Sea is weak (Qiao, 2012). However, large amounts of nutrients and pollutants enter the Bohai Sea annually through rivers, direct sewerage discharge and atmosphere deposition resulting in severe environmental problems in recent decade (Bulletin of Marine Environmental Status of China, 2014). The Bohai Economic Rim (BER, encompassing Beijing, Tianjin, Shandong Province, Hebei Province and Liaoning Province) has been the essential economy center with rapid development in the North China and subsequently it has become the largest BC emission region in China (Cao *et al.*, 2006; Wang *et al.*, 2012). Concentrations of BC in the surface sediment of the Bohai Sea (27% −41% of sediment organic carbon) are much higher than those in other Chinese seas (5% −8% of sediment organic carbon) and other coastal zones around the world (5% − 38% of sediment organic carbon) (Forbes *et al.*, 2006; Kang *et al.*, 2009). However, to the best of our knowledge, no attention has been paid on the DBC for the Bohai Sea. The objective of this study is to investigate the concentrations, temporal-spatial variations of DBC in the Bohai Sea to help us better understand the sources-sinks process of BC in the North China.

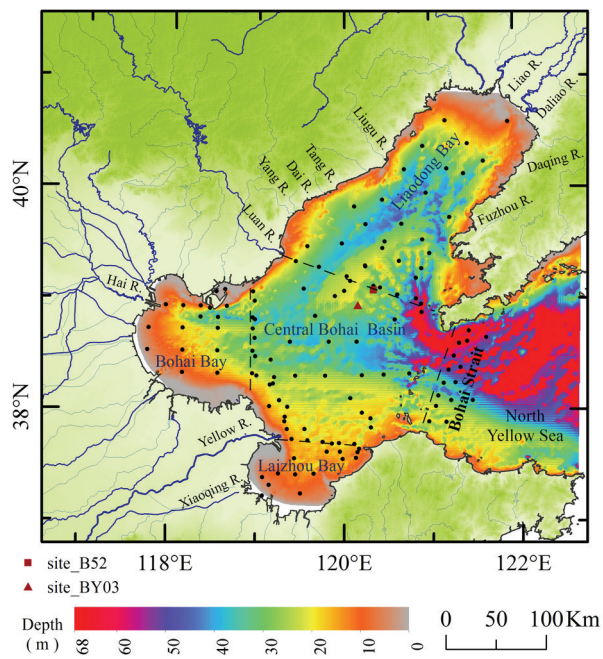

Figure 1. Map showing the study area and sampling sites

MATERIALS AND METHODS

Sample collection

The seawater samples were collected in six cruises from 2010 to 2014 (Figure 1). Four cruises were from April 30 to May 3 in 2010, from September 16 to 20 in 2010, from June 24 to 28 in 2011 and from November 25 to December 1 in 2011 in the open cruises of the Bohai Sea and the Yellow Sea for multidisciplinary oceanographic observations supported by the National Science Foundation of China (NSFC), deployed by the Research Vessel-*Dong Fang Hong* 2. These four cruises represented spring, autumn, summer and winter, and a total of 357 seawater samples were collected on 68 sampling sites in three layers (surface, middle and bottom layers) locating in the Central Bohai Basin and the Bohai Strait. Additional 72 samples were taken in 36 sites (surface and bottom layers) in the Bohai Bay and the Laizhou Bay from September 23 to October 17 in 2013, using the Research Vessel-*HaoHai*. In Liaodong Bay, 66 samples were collected in 22 sites (surface, middle and bottom layers) from August 12 to September 5 in 2014 by R/V*HaoHai*. The seawater

was sampled using Niskin bottles couple with a CTD system. Physicochemical parameters (water salinity, temperature, depth and pH) were measured *in situ* by CTD.

Sample preparation

Several methods have been reported for DBC measurement, such as CTO-375 and Fourier transformion cyclotron resonance (FTICR) mass spectrometer (Dittmar and Koch, 2006; Kim *et al.*, 2004; Mannino and Harvey, 2004). Benzene polycarboxylic acid (BPCA) method is a molecular marker method for BC and DBC analysis (Brodowski *et al.*, 2005; Glaser *et al.*, 1998). After revising by Dittmar (2008), BPCA method became the first choice for DBC analysis and has been used for large amount of samples (Ding *et al.*,2013; Ding *et al.*, 2014; Ding *et al.*, 2015; Dittmar, 2008; Dittmar *et al.*, 2012a; Dittmar *et al.*, 2012b; Dittmar and Paeng, 2009; Jaffé *et al.*, 2013). Therefore, BPCA method was chosen to measure DBC in this work.

After sampling, the water was filtered through pre-combusted Whatman quartz membrane filters(nominal poresize 0.7 μm) and acidified with HCl(32%) to pH = 2. DBC was isolated from 1 L seawater via solid phase extraction (SPE) using Supelco Supelclean ENVI-Chrom P (500mg) cartridges (Reorder NO. 57226).

New cartridges were rinsed with 10 mL of methanol (HPLC grade) before use. The filtered and acidified water were pumped through the cartridges at a flow rate of <5 mL min^{-1}. After adsorption, the cartridges were washed off the salts with 20 mL of acidified water (pH = 2), dried under the air stream and stored at -20℃ until elution. 10 mL of methanol was used for eluting DBC and the eluate was condensed to nearly dryness using nitrogen gas flow and then transferred to 2 mL polytetrafluoroethylene (PTFE) digestion tube. After re-drying in the tube, 0.5 mL of concentrated nitric acid (65%) was added for acid digestion. The tubes were sealed and heated to 170℃ for 7 hours in an oven. After digestion, the samples were dried in the PTFE tubes with nitrogen gas flow at 50℃ to remove nitric acid and water. 1 mL of methanol/water mixture (50∶50, V/V) was used to re-dissolve the digestion products. 10 μg of biphenyl-2, 2'-dicarboxylic acid (2 μg μL^{-1} in methanol) as internal standard for quantification was added and the sample was transferred to vial for HPLC analysis.

Sample analysis

BPCA standard compounds (B6CA, B5CA, 1,2,4,5-B4CA, 1,2,3-B3CA, 1,2,4-B3CA and 1,3,5-B3CA) were purchased from Sigma-Aldrich (USA) while prehnitic acid and mellophanic acid (1,2,3,4-B4CA and 1,2,3,5-B4CA) were not commercially available. One nitro-benzenetricarboxylic acid standard compound (5-nitro-1, 2, 3-B3CA) was purchased from Hangzhou Elion Chemical Industrial Co., Ltd. (China). However the other nitro-benzenecarboxylic acids (nitro-B4CAs and nitro-B3CAs) were not available recently. Internal standard (biphenyl-2, 2'-dicarboxylic acid) was also purchased from Sigma-Aldrich. A series of standard solutions were prepared for quantification with concentrations of 1, 2, 5, 10, 20, 50 and 100 μg μL^{-1} with a constant internal standard concentration of 10 μg μL^{-1}. Target compounds' chemical names, abbreviated names and their quantification of standard curves are listed in Table 1.

Table 1. *Target compounds' names and their standard curves for quantification*

Chemical name	Abbreviation	Standard curve for quantification
1,2,3,4,5,6-Benzenehexacarboxylic acid	B6CA	B6CA
1,2,3,4,5-Benzenepentacarboxylic acid	B5CA	B5CA
1,2,3,4-Benzenetetracarboxylic acid*	1,2,3,4-B4CA	1,2,4,5-B4CA
1,2,4,5-Benzenetetracarboxylic acid	1,2,4,5-B4CA	1,2,4,5-B4CA
1,2,3,5-Benzenetetracarboxylic acid*	1,2,3,5-B4CA	1,2,4,5-B4CA
3-nitro-1,2,4,5-Benzenetetracarboxylic acid*	3-nitro-1,2,4,5-B4CA	1,2,4,5-B4CA
5-nitro-1,2,3,4-Benzenetetracarboxylic acid*	5-nitro-1,2,3,4-B4CA	1,2,4,5-B4CA
1,2,3-Benzenetricarboxylic acid	1,2,3-B3CA	1,2,3-B3CA
1,2,4-Benzenetricarboxylic acid	1,2,4-B3CA	1,2,4-B3CA
1,3,5-Benzenetricarboxylic acid	1,3,5-B3CA	1,3,5-B3CA
4-nitro-1,2,3-Benzenetricarboxylic acid*	4-nitro-1,2,3-B3CA	5-nitro-1,2,3-B3CA
5-nitro-1,2,3-Benzenetricarboxylic acid	5-nitro-1,2,3-B3CA	5-nitro-1,2,3-B3CA
3-nitro-1,2,4-Benzenetricarboxylic acid*	3-nitro-1,2,4-B3CA	5-nitro-1,2,3-B3CA
5-nitro-1,2,4-Benzenetricarboxylic acid*	5-nitro-1,2,4-B3CA	5-nitro-1,2,3-B3CA
6-nitro-1,2,4-Benzenetricarboxylic acid*	6-nitro-1,2,4-B3CA	5-nitro-1,2,3-B3CA
Biphenyl-2,2'-dicarboxylic acid#	—	—

* Not commercially available; #Internal standard.

BPCA method is a molecular marker method and its basic principle is that the condensed aromatic structures were broken down to single aromatic rings substituting by different numbers (two to six) of carboxylic which were named benzene polycarboxylic acids during the nitric aciddigestion (Glaser *et al.*, 1998). What's more, nitro-benzene polycarboxylic acids (nitro-BPCAs) were produced besides BPCAs (Glaser *et al.*, 1998). Recently, it has been showed that the amount of nitro-BPCAs was remarkable and thus they can't be ignored (Ziolkowski *et al.*, 2011). Dittmar (2008) developed a HPLC method for separation of BPCAs via a reversed phase HPLC column while the elution was modified with quaternary ammonium salt. However this method can't detect nitro-BPCAs due to lacking of standard compounds and incompatible to mass spectrometer detector (MS). Mass spectrometry can qualify the target compounds although standards aren't available. Herein an alternative HPLC separation method was developed which is compatible to MS for detecting BPCAs and nitro-BPCAs simultaneously.

An ether-linked phenyl with polar end-capping HPLC column (Synergi, 4 μm Polar-RP 80 Å, 250 × 4.6 mm, Phenomenex, USA) was used. It's a reversed phase column suitable to separate polar, aromatic compounds because of the ether bond and the polar end-capping. BPCAs and nitro-BPCAs were well separated with gradient elution. Two mobile phases were used: 0.5% (V/V) formic acid in water (A) and methanol (B); The other parameters were column temperature: 35℃; Flow rate: 0.5 mL min^{-1}; Injection volume: 10 μL; Mobile phase gradients: 5% of phase B as initial condition, held for 10 minutes, raising phase B to 40% at 40 minute, 85% at 50 minute, and kept to 55 minute. Additional 30 minutes was used to clean and balance the column for next injection.

When target compounds were confirmed by HPLC-MS, several hundreds of samples were separated and quantified in a Waters Alliance E2695 HPLC system couple with a Photo-Diode Array-Detector (DAD). The UV wave length range was 210 nm to 400 nm and 240 nm chromatogram was extracted for quantification (Dittmar2008). Each compound was confirmed with retention time and absorbance spectra. A standard sample (5μg μL^{-1}) was run after every 10 sample runs for quality control (QC). Retention times were very stable and reproducible within 1 min window during 3 months of analysis. And approximately 300 runs were conducted using the same HPLC column. The detection limitation was 5μg per injection. Blank sample analysis showed no detectable target compounds. Method reproduction was estimated by 20 samples doubly and the results showed that the relative average deviations were 0.1% to 12.8% with a mean value of 4.6 ±3.6%.

All BPCAs including nitro-BPCAs with three or more carboxylic groups were operationally defined as DBC, while B2CAs were not quantified because they may be derived from processes other than incomplete combustion, *e. g.*, lignin and humic materials. Some compounds without standard were semi-quantified by the analogous standard compound calibration curves. For instant, the curve of 5-nitro-1,2,3-BPCA was used to quantify all nitro-B3CAs (5 compounds); the curve of 1,2,4,5-B4CA was used to quantify 1,2,3,4-B4CA, 1,2,3,5-B4CA and two nitro-B4CAs (Table 1). The BPCA method requires a conversion factor to convert the mass of BPCA-C to an estimate of total DBC mass in the original sample. A conversion factor of 25.8 ± 6.8% C (Ziolkowski *et al.*, 2011) was used in this work.

Spatial geostatistical analysis

Spatial interpolation is often used to predict a value of a variable of interest at unmeasured locations from the available measurements at sampled sites. It is one of the most often used geographic techniques for spatial data visualization, spatial query of properties and spatial decision-making processes in geography, earth sciences and environmental science (Meng *et al.*, 2013). To analyze the DBC spatial distribution, kriging method was used for interpolation from our scattered set of sample sites by ArcGIS. Kriging is a kind of geostatistical methods which are based on statistical models that include autocorrection, that is, the statistical relationships among the measured points (ArcGIS Help 10.1. http://resources.arcgis.com/en/help/main/10.1/).

RESULTS

Concentrations of DBC

The concentrations of DBC in the entire Bohai Sea ranged from 36.5 to 208.3 μg L^{-1} with a mean value of 96.6 ± 32.9 μg L^{-1} (n = 495), while the average concentrations of DBC in the Laizhou Bay (LZB), Bohai Bay (BHB), Liaodong Bay (LDB), Central Bohai Basin (CBHB) and Bohai Strait (BHS) were 136.2 ± 33.7 (n = 28), 131.2 ± 30.3 (n = 44), 86.3 ± 16.1 (n = 66), 89.6 ± 19.8 (n = 277) and 57.8 ± 8.6 μg L^{-1} (n = 80) respectively (Table 2).

The average DBC concentrations of the surface, middle and bottom layers were 87.2 ± 20.8 (n = 95), 84.5 ± 17.7 (n = 88) and 86.8 ± 21.3 μg L^{-1} (n = 94) in the CBHB; 58.7 ± 11.8 (n = 27), 57.9 ± 11.2 (n = 27) and 54.9 ± 12.0 μg L^{-1} (n = 26) in the BHS; 90.6 ± 19.3 (n = 22), 86.4 ± 17.9 (n = 22) and 81.9 ± 15.5 μg L^{-1} (n = 22) in the LDB. And the average DBC concentrations of the surface and bottom layers were 134.2 ± 33.8 (n = 14) and 138.1 ± 33.5 μg L^{-1} (n = 14) in the LZB; 130.1 ± 30.6 (n = 22) and 132.3 ± 30.1 μg L^{-1} (n = 22) in the BHB (Table 2).

The average DBC concentrations of spring, summer, autumn and winter were 83.2 ± 10.2 (n = 66), 82.8 ± 22.2 (n = 97), 91.5 ± 19.6 (n = 45) and 90.5 ± 22.6 μg L^{-1} (n = 69) in the CBHB; 51.2 ± 5.9 (n = 27), 49.8 ± 5.2 (n = 12), 58.1 ± 11.8 (n = 26) and 72.4 ± 8.7 μg L^{-1} (n = 15) in the BHS (Table 2).

Figure 2 compared the concentrations of DBC in different areas around the world. It showed that the concentration of DBC in the Bohai Sea was much higher than those in the open ocean, *e. g.* the Southern Ocean (Dittmar and Paeng, 2009), North Atlantic and Northeast Pacific (Ziolkowski and Druffel, 2010); comparable to those in other coastal zone water, *e. g.* the Gulf of Mexico (Dittmar *et al.*, 2012b); lower than those in rivers, *e. g.* the Suwannee River (Ziolkowski and Druffel, 2010).

Table 2. *Concentrations of DBC in the Bohai Sea* ($\mu g\ L^{-1}$)

	n	mean	Std. Dev.	min	1−st Quartile	Median	3−st Quartile	max
Laizhou Bay Sur.	14	134.2	33.8	77.4	108.8	131.8	167.2	184.0
Laizhou Bay Bot.	14	138.1	33.5	90.6	106.2	133.3	180.2	191.6
Laizhou Bay Tot.	28	136.2	33.7	77.4	107.4	131.8	171.6	191.6
Bohai Bay Sur.	22	130.1	30.6	65.9	108.2	126.1	148.9	188.9
Bohia Bay Bot.	22	132.3	30.1	83.9	105.9	134.0	152.5	208.3
Bohai Bay Tot.	44	131.2	30.3	65.9	106.8	130.7	151.7	208.3
Liaodong Bay Sur.	22	90.6	19.3	61.6	79.0	90.4	98.6	154.4
Liaodong Bay Mid.	22	86.4	17.9	38.2	81.7	88.1	95.9	127.6
Liaodong Bay Bot.	22	81.9	15.5	44.4	71.1	84.3	92.1	111.6
Liaodong Bay Tot.	66	86.3	16.1	38.2	80.2	88.9	93.3	154.4
Central Bohai Basin Sur.	95	87.2	20.8	44.5	73.0	85.7	98.5	143.0
Central Bohai Basin Mid.	88	84.5	17.7	48.2	74.4	83.2	94.6	135.2
Central Bohai Basin Bot.	94	86.8	21.3	47.7	73.5	85.4	97.8	151.9
Central Bohai Basin Spr.	66	83.2	10.2	55.5	76.7	82.6	90.1	102.7
Central Bohai Basin Sum.	97	82.8	22.2	47.7	67.0	76.7	94.2	151.9
Central Bohai Basin Aut.	45	91.5	19.6	51.9	74.2	94.0	106.9	133.0
Central Bohai Basin Win.	69	90.5	22.6	44.5	77.4	87.1	102.0	143.6
Central Bohai Basin Tot.	277	89.6	19.8	44.5	74.6	86.4	98.9	151.9
Bohai Strait Sur.	27	58.7	11.8	37.1	49.7	54.3	70.7	87.3
Bohai Strait Mid.	27	57.9	11.2	40.8	47.5	55.2	67.5	86.2
Bohai Strait Bot.	26	54.9	12.0	36.5	48.1	51.7	62.7	82.0
Bohai Strait Spr.	27	51.2	5.9	37.1	48.3	49.5	54.0	64.4
Bohai Strait Sum.	12	49.8	5.2	39.1	46.4	52.0	54.1	55.2
Bohai Strait Aut.	26	58.1	11.8	36.5	49.5	58.7	68.4	79.2
Bohai Strait Win.	15	72.4	8.7	54.8	67.7	72.2	76.7	87.3
Bohai Strait Tot.	80	57.8	8.6	36.5	48.8	54.6	68.4	87.3
Entire Bohai Sea	495	96.6	32.9	36.5	72.4	90.2	116.3	208.3

Sur. : Surface layer; Mid. : Middle layer; Bot. : Bottom layer; Tot. : Total; Spr. : Spring; Sum. : Summer; Aut. : Autumn; Win. : Winter

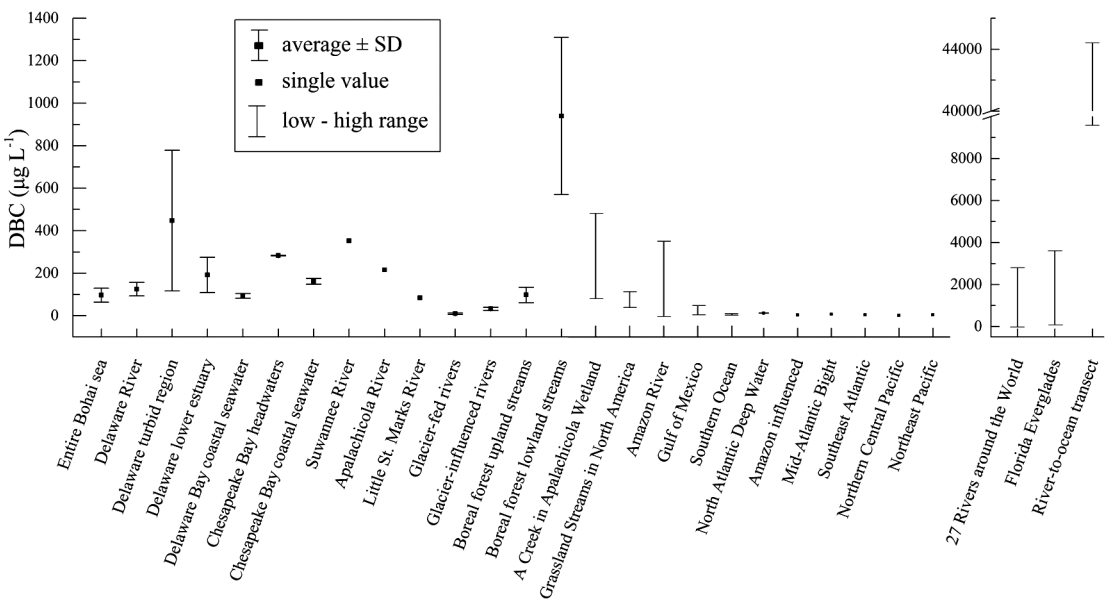

Figure 2. Comparison of DBC concentrations in different areas around the world
Figure was plotted based on the data from the references: Ding *et al.*, 2013; Ding *et al.*, 2014; Ding *et al.*, 2015; Dittmar, 2008; Dittmar *et al.*, 2012a; Dittmar *et al.*, 2012b; Dittmar and Paeng, 2009; Jaffé *et al.*, 2013; Ziolkowski and Druffel, 2010

DISCUSSION

Distribution and seasonal variations of the DBC concentrations in the CBHB and BHS

The DBC concentrations in the vertical layers showed little variations ($p > 0.1$). The average DBC concentrations of the surface, middle and bottom layers were comparable in the CBHB and the same to those in the BHS. The DBC distribution patterns of the surface, middle and bottom layers were similar in the same season except for the summer bottom layer (Figure 3). Similar phenomenon was also found in the three bays. The average water depth of the CBHB and the BHS is 22 m. In this shallow sea, the water column can mix well by waves and tides, so it was reasonable for little vertical variations of the DBC concentrations. However in summer the sea condition is calm except for typhoon events period and the solar radiation is much stronger than other seasons. Because of these two reasons, the Bohai Sea stratifies in most areas except near the coast in summer (Lin *et al.*, 2006), and then we saw that the summer bottom layer's DBC distribution pattern was different from the summer surface and middle layers'.

On the contrary, The DBC concentrations varied largely in the horizontal direction (Figure 3). It was clear to see that DBC concentrations were lower in the BHS than those in the areas adjacent to the Bays. For example, in spring the average DBC concentration was 52.3 ± 5.1 μg L^{-1} ($n = 24$) in the Bohai Strait transect while it was 90.4 ± 10.2 ($n = 15$) in the Bohai Bay mouth transect.

The patterns of DBC concentrations in four seasons showed distinct difference (Figure 3). The seasonal variations of the DBC concentrations indicated the water exchange processes between the Bohai Sea and the North Yellow Sea, because the Bohai Strait is the only exchange channel for the two seas and the DBC concentrations in the Bohai Sea water were much higher than that in the North Yellow Sea water.

In spring, there was a low DBC concentration region which started from the Bohai Strait extending southwest to the Laizhou Bay. This character indicated that the outer sea water invaded the Bohai Sea from the south of the Bohai Strait and then flowed to southwest reaching the mouth of Laizhou Bay, which was consistent with "inflow in the south and outflow in the north of the Bohai Strait in spring" proposed by Hainbucher *et al.* (2004). The water salinity and temperature analysis showed that there was relative high salinity water mass spreading from the North Yellow Sea to the south of the Bohai Strait, which co-supported the above conclusion (Figure 4).

The DBC distribution pattern of the bottom layer in summer was similar to that in spring while the patterns of the surface and middle layers between these two seasons were different. This character suggested that the water exchange remained the main style of spring in bottom layer but changed from the middle layer to the surface layer. In the surface and middle layers, there were low DBC concentration regions both in the south and in the north of the Bohai Strait and a notable ring zone with higher DBC concentration located at 39°N, 121°E with a diameter about 70 km in north of the CBHB. The DBC concentration was 130.0 μg L^{-1} in the center while it was 70.0 to 80.0 μg L^{-1} outside the zone. These characters indicated that the outer seawater invaded the Bohai Sea from two main paths: the south flow and the north flow, and formed an eddy in the north of CBHB. Lin *et al.* (2002) proposed that in summer (August) water inflow was observed nearly the whole Bohai Strait from the surface to subsurface layer but it was stronger in the south and the north parts than in the middle part of the Bohai strait (Figure 5), notably the north inflow was the strongest above 30 m but weak in the bottom. This ocean current structure supported our DBC distribution patterns of the three layers near the Bohai Strait. Lin *et al.* (2006) demonstrated that there was a warm water column in the same position of high DBC concentration in north of the CBHB based on the data of temperature and salinity from multi-years (1976 −2000), and the warm water column is anchored by a sea-bottom ridge (Figure 1) with water depth slightly less than 20 m. Our water temperature and salinity data also supported this phenomenon (Figure 5). Sampling sites BY03 (21m water depth) and B52 (22m water depth) were located in the center of the warm water column (Figure 1), and their surface, middle and bottom layer water temperature were 17.67, 17.47 and 17.47℃; 18.56, 18.23 and 17.58℃, respectively; their surface, middle and bottom layer water salinity were 31.156, 31.148 and 31.156 PSU; 31.227, 31.220, and 31.223 PSU, respectively. These small temperature and salinity variations suggested a well-mixed water column. On the contrary, the water temperature decreased and salinity increased from surface to bottom on other sample sites, for instance, the surface, middle and bottom layers water temperature were 18.95, 14.29 and 13.57℃ in the site BY02 (28m water depth) and their salinity were 30.953, 31.294 and 31.337 PSU. Therefore, higher DBC concentration and warm water column clearly proved that an eddy was formed and its source was coastal water mass. The special sea-floor ridge, currents, waves and tide were the indispensable factors for the notable eddy forming in summer (Lin *et al.*, 2006).

In autumn, low DBC concentration region started from the north of the Bohai Strait and extended forward northwest to the LDB, which was inverse comparing to that in spring. The low DBC concentration water mass coincided with the relatively low temperature and high salinity water mass in the middle and bottom layers although its surface water had relatively high temperature and low salinity (Figure 6). This pattern of DBC distribution indicated that the outer seawater invaded the Bohai Sea from the North Bohai Strait and then flowed towards northwest reaching the LDB. The southern inflow in summer disappeared but the northern one still remained. Autumn was the transition period from summer type to winter type for water exchange patterns through the Bohai Strait (Lin *et al.*, 2002). Therefore the pattern of "inflow in the north and outflow in the south of the Bohai Strait" began to form in autumn.

In winter, the DBC distribution pattern showed low value in the north and high value in the south of the Bohai Strait, similar to the DBC distribution of autumn. Many researchers have found that the water exchange in the Bohai Strait has marked character of "inflow in the north and outflow in the south" in winter (Fang *et al.*, 2000; Lin *et al.*, 2002; Zhang *et al.*, 2010). The outflow is a strong coastal current named the North Shandong Coastal Current which flows along the southwest shore of BHB and LZB and exits from Bohai Sea through the south Bohai Strait. A belt-shape zone with higher DBC concentration, lower salinity and temperature was observed that coupled with the North Shandong Coastal Current flow path (Figure 7). The DBC distribution pat-

tern of winter also well exhibited the ocean currents like other seasons. Moreover, in winter the concentrations of DBC in the CBHB and the BHS were higher than those in other seasons (Table 2, Figure 3). The main reason is that hydrodynamics of the Bohai Sea is significantly affected by the East Asia Monsoon (Wang *et al.*, 2014), and the northerly or northwesterly wind is very strong in winter resulting in faster seawater exchange between the bays and the CBHB in winter than other seasons. Therefore higher DBC concentrations in the CBHB and the BHS were observed.

As discussed above, the DBC distribution patterns correlated well with the ocean currents, suggesting that DBC would be a potential marker for the study of the regional hydro-dynamics processes.

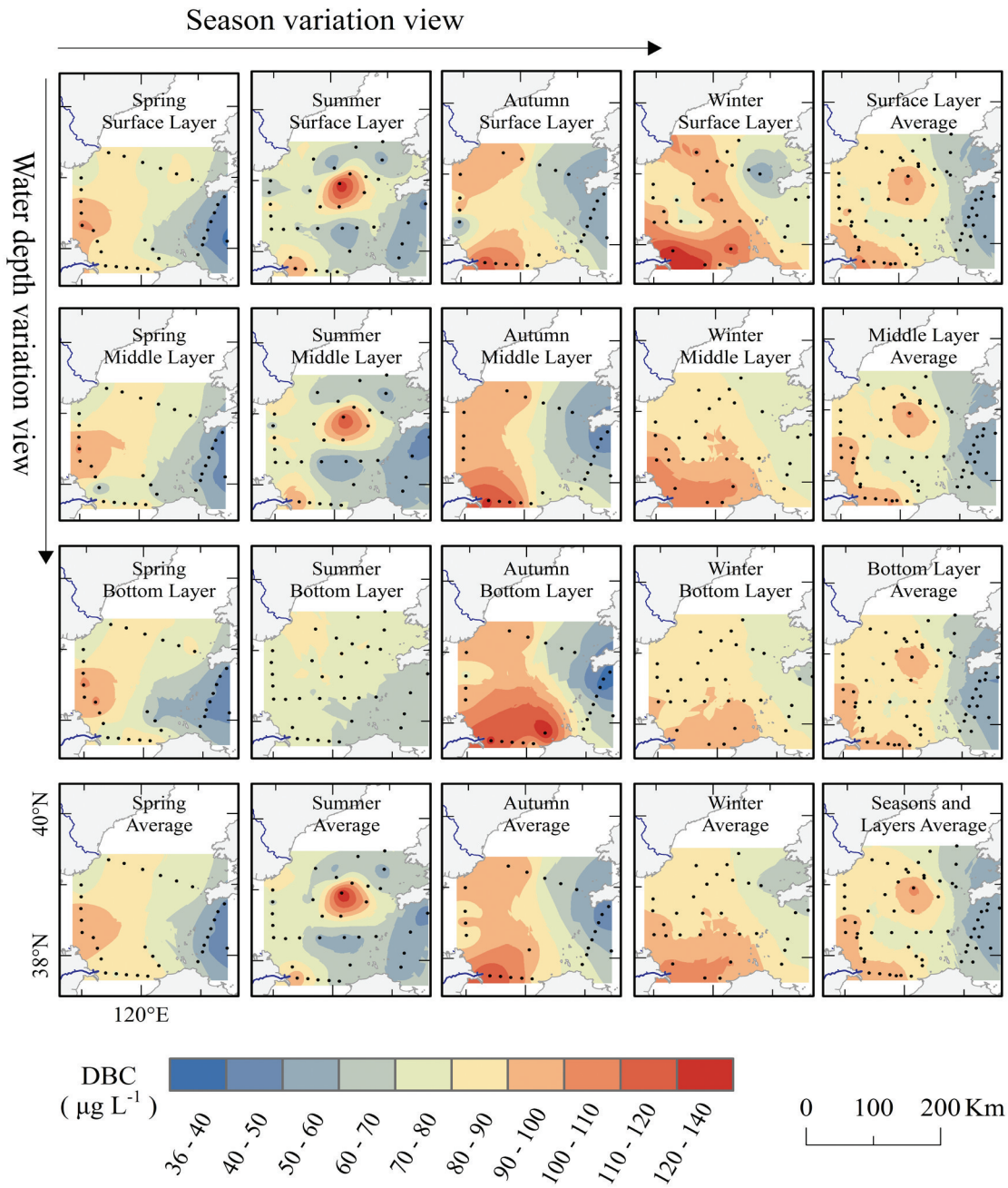

Figure 3. Seasonal and spatial distributions of DBC in the Central Bohai Basin and the Bohai Strait

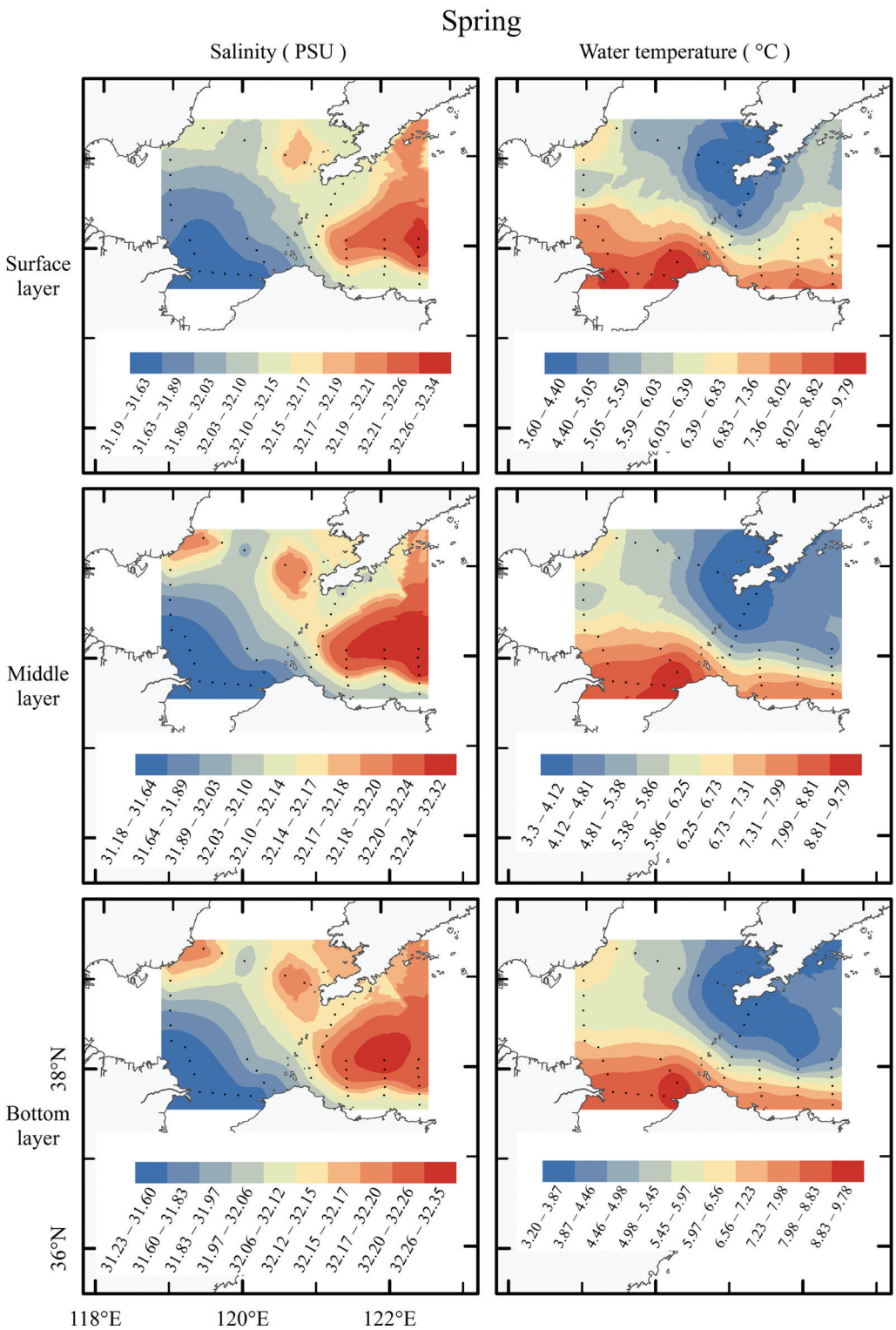

Figure 4. Water salinity and temperature in spring cruise of the Bohai Sea

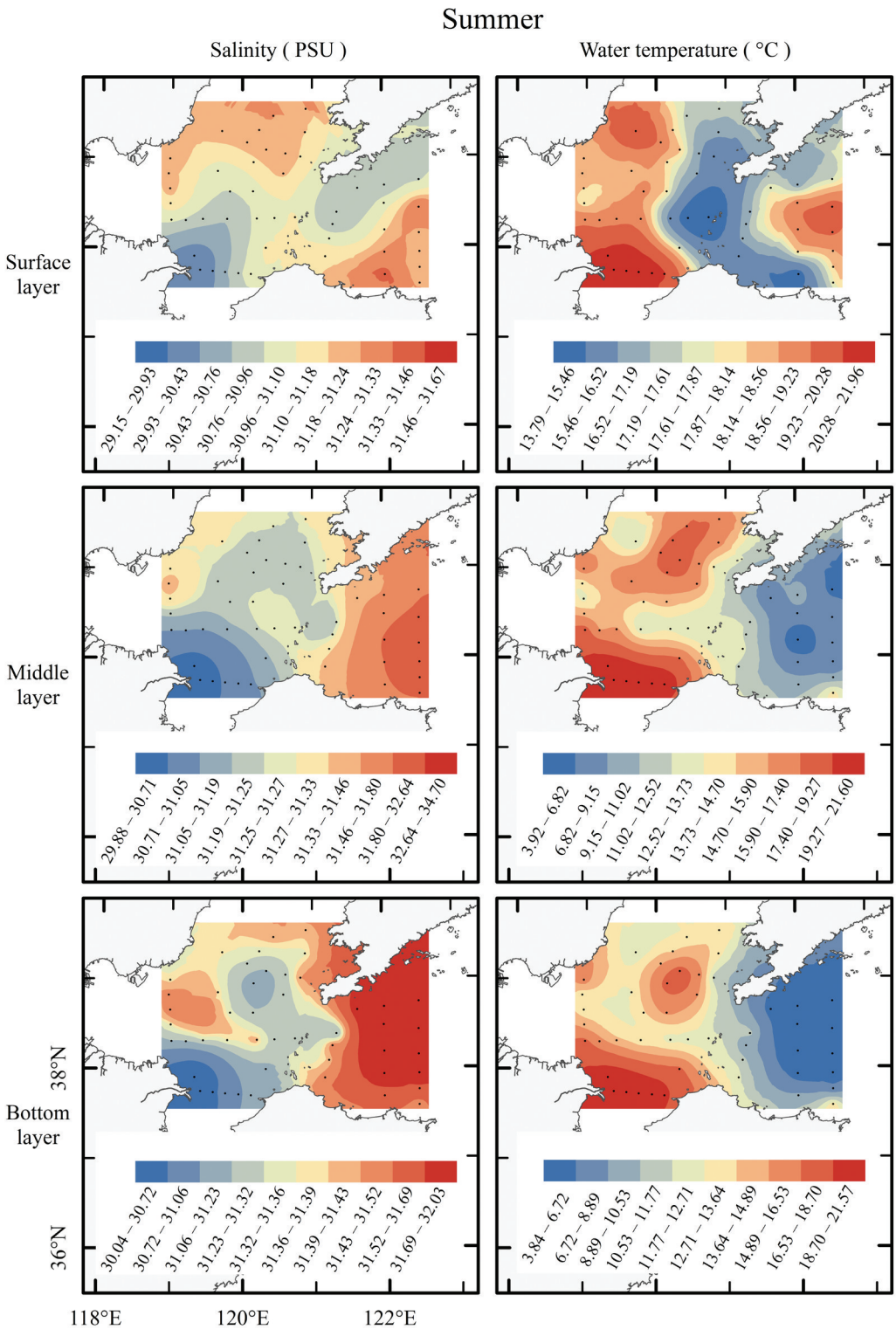

Figure 5. Water salinity and temperature in summer cruise of the Bohai Sea

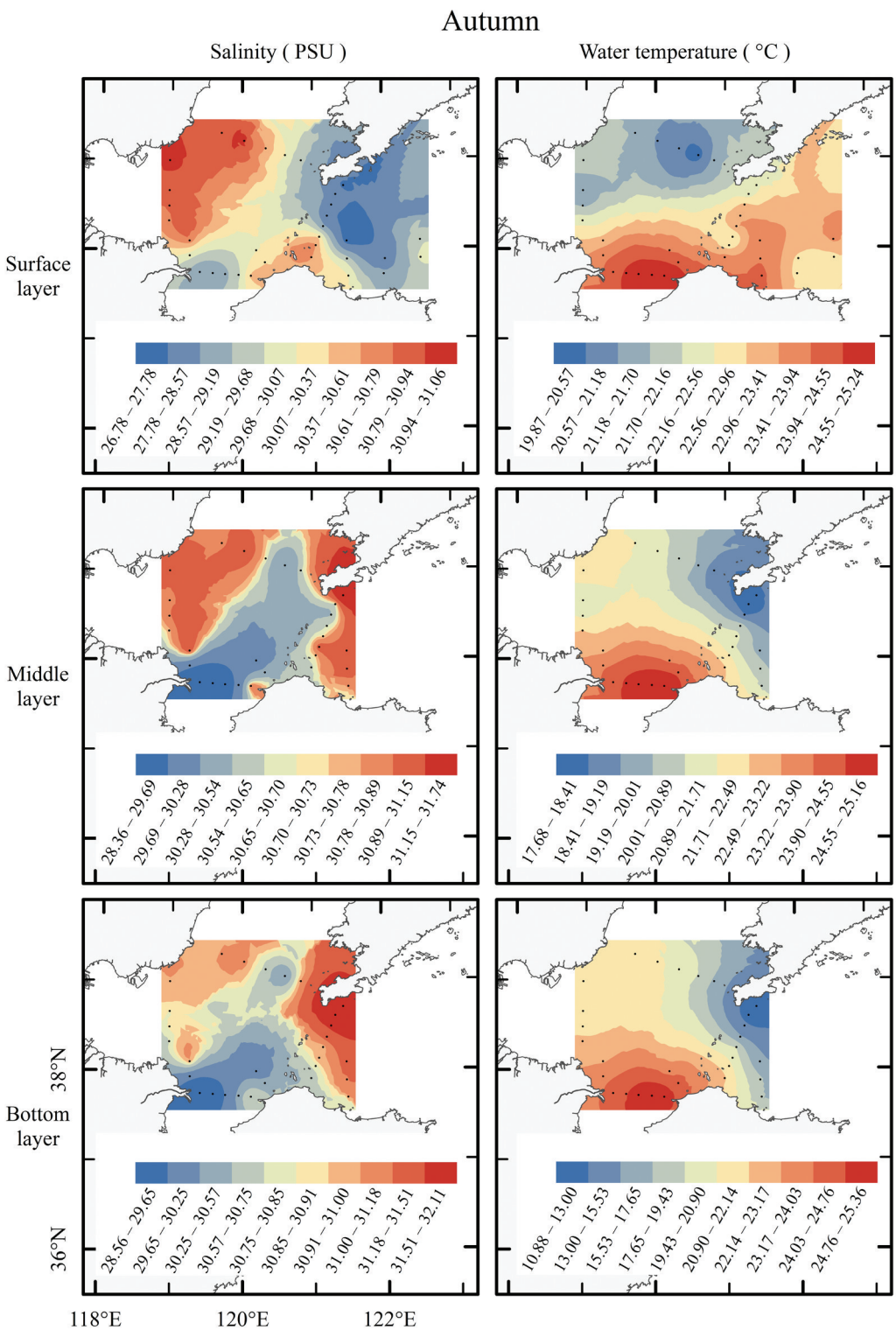

Figure 6. Water salinity and temperature in autumn cruise of the Bohai Sea

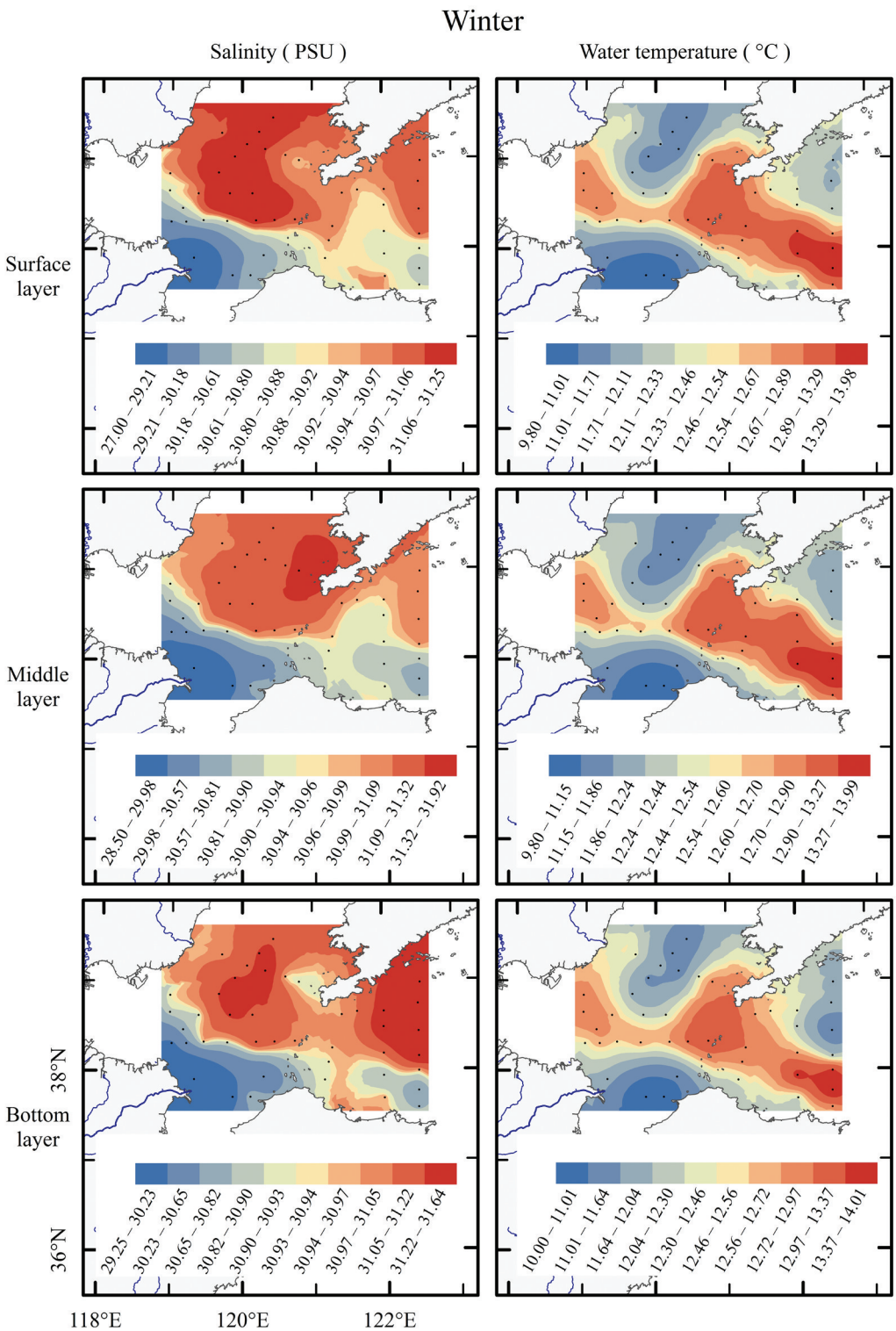

Figure 7. Water salinity and temperature in winter cruise of the Bohai Sea

Horizontal distribution of DBC in the entire Bohai Sea

Figure 8 showed the horizontal distribution of DBC in the entire Bohai Sea. It was plotted by kriging interpolation method compiling DBC average concentrations of different layers and seasons in each site. Three prominent features, i. e. highest DBC concentration on the top of bays, lowest DBC concentration in the BHS and a solitary region with relative higher DBC concentration in north of the CBHB, were observed. DBC concentrations showed a distinct decreasing trend from coastal area to offshore area and from internal Bohai Sea to the Bohai Strait.

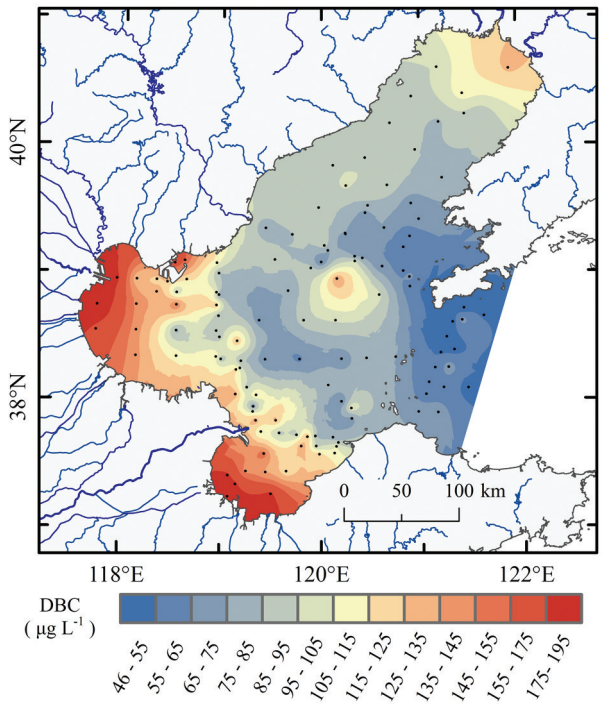

Figure 8. The distribution of DBC concentrations in the entire Bohai Sea

DBC showed the highest concentration on top of the BHB and LZB, reaching up to 190 μg L^{-1}, and decreased nearly linearly to about 100 μg L^{-1} on the mouth of the two Bays along the salinity increasing (Pearson's correlation coefficient were −0.76 and −0.85 respectively, Figure 9). In the BHB, there is Hai River drainage system. And the main rivers, Jiyun River, Yongding new River, Hai River and Duliujian River enter the BHB in the northern coast. Correspondingly, DBC concentrations were higher in the northern coast than those in the southern coast. Similarly there are several rivers entering the LZB in the southern coast, which resulted in higher DBC concentrations in the southern coast than the eastern and the western coast.

The highest DBC concentration in the LDB also occurred on the top of the Bay with the value of 150 μg L^{-1}, but lower than those in the BHB and the LZB. Liao River and Daliao River are the two largest rivers entering the LDB on the north top where the highest DBC concentrations zone appeared. DBC concentrations decreased from the top to the mouth of the LDB like the BHB and the LZB. Additionally, higher DBC concentrations in the western coast rather than in the eastern coast were observed in the LDB. This feature was attributed to the facts that the riverine flux of DBC was larger and the water exchange was weaker in the western than eastern of the LDB. There are Liugu River, Tang River, Dai River and Yang River in the western coast while only Fuzhou River and Daqing River in the eastern coast. And the eastern coast of the LDB is nearer to the BHS which is the inflow channel of the outer seawater (Figure 1).

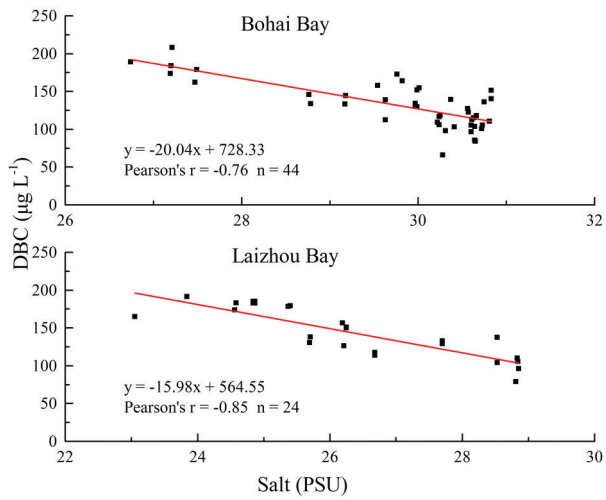

Figure 9. Relation between DBC concentration and salinity in the Bohai Bay and Laizhou Bay

The DBC concentrations were lower in the CBHB than those in the Bays because the water exchange ability with outer seawater was stronger and there was no riverine DBC input directly in the CBHB (Hainbucher *et al.*, 2004). The DBC concentrations were lower than 90 μg L^{-1} in most areas of the CBHB while a high value region existed. The high value region was mainly attributed to high DBC concentrations in summer in the warm water column (discussed above). There were two low DBC concentration areas which started in the Bohai Strait, one meandered northward and the other one meandered southward. And the northward one had lower DBC concentrations than the southward one. This indicated that the outer seawater flowed into the Bohai Sea from two directions and the northward path was stronger than the southward path in yearly scale.

The Huang River (Yellow River) is the biggest river among the rivers entering the Bohai Sea. Its water flux contributes to nearly 50% of the total river flux to the Bohai Sea (Wang *et al.*, 2006). And there was a water tongue with higher DBC concentration at the mouth of the Huang River, indicating the diluted water spreading direction and range.

The DBC concentrations, horizontal distribution expressed the general transport paths and features of DBC within the complex hydro-dynamics after it arrived to the Bohai Sea coastal area. DBC mainly comes from terrestrial soil and then transports to the sea through rivers and underground water (Guggenberger *et al.*, 2008; Mitra *et al.*, 2014). Therefore, the distribution features

and the transport routes of DBC shown in this study would provide some useful information for other pollution risk assessment and management in the Bohai Sea water.

CONCLUSIONS

The concentrations, distribution and seasonal variations of DBC in the Bohai Sea were studied systematically for the first time. The average concentration of DBC was 96.6 ± 32.9 μg L^{-1} (n = 495) in the entire Bohai Sea, comparable to those in other coastal zone water bodies. The sub-regional means of DBC concentrations within the study area were 136.2 ± 33.7 μg L^{-1} (n = 28) in the LZB, 131.2 ± 30.3 μg L^{-1} (n = 44) in the BHB, 86.3 ± 16.1 μg L^{-1} (n = 66) in the LDB, 84.2 ± 20.6 μg L^{-1} (n = 277) in the CBHB and 57.8 ± 8.6 μg L^{-1} (n = 80) in the BHS. DBC concentrations decreased distinctly form coastal area to off shore area, from internal Bohai Sea to the Bohai Strait although no significant difference ($p > 0.1$) was observed in the vertical water column because the water depth was shallow enough to mix well.

The average DBC concentrations in spring, summer, autumn and winter were 83.2 ± 10.2 (n = 66), 82.8 ± 22.2 (n = 97), 91.5 ± 19.6 (n = 45) and 90.5 ± 22.6 μg L^{-1} (n = 69) in the CBHB; 51.2 ± 5.9 (n = 27), 49.8 ± 5.2 (n = 12), 58.1 ± 11.8 (n = 26) and 72.4 ± 8.7 μg L^{-1} (n = 15) in the BHS. The average DBC concentrations of the four seasons were comparable. However the seasonal DBC concentration distributions differed largely and followed well with the seasonal variations of the ocean currents. This suggested that DBC would serve as a potential marker for the hydro-dynamics study.

The DBC concentration distributions and seasonal variations expressed the general transport paths and characters of DBC within the complex hydro-dynamics after it arrived to the Bohai Sea coastal area. This study can be acted as an example for other pollutions investigations and their translocation process researches. High level of DBC (up to 100 μg L^{-1}) has been detected in the Bohai Sea, which may have resulted in adverse effects on the environment and ecology. Unfortunately no knowledge was gained about this. More researches are needed to well understand the fate and the effects of DBC in the Bohai Sea.

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